

Supplementary Information

**Temperature Control of
Photoreaction for Hydrogen Generating Gel Systems**

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(S1)

Experimental details.

Materials. *N*-isopropylacrylamide (NIPAAm; Wako Pure Chemical Industries, Co., Ltd., Osaka, Japan) was purified by recrystallization from its toluene solution with hexane. Ruthenium(4-ninyl-4-methyl-2,2'-bipyridine)bis(2,2'-bipyridine)bis(chloride) (Ru(bpy)₃ monomer) was synthesized according to previous work.^[1] Other reagents were used without further purification.

Preparation of Gels. Firstly, surfactant-modified Pt nanoparticle was prepared by alcohol reduction method^[2] with chloroplatinic acid (H₂PtCl₆·6H₂O; Wako Pure Chemical Industries, Co., Ltd., JAPAN) (34 mg), reactive surfactant (S180A; Kao Co., JAPAN) (380 mg)^[3] as a protector and ethanol-water mixed solvent (30 mL / 30 mL). After centrifugation, the colloidal solution was concentrated and dispersed in water (6.0 mL). The diameter of the S180A-Pt nanoparticles were about 2-3 nm from the observation of transmission electron microscopy.^[4] Secondly, NIPAAm (478 mg), Pt-colloidal solution (0.10 mL), Ru(bpy)₃ monomer (22 mg), *N,N'*-methylenebisacrylamide as a cross-linker (13 mg), and *N,N,N',N'*-tetramethylenediamine (100 μL) as an accelerator were dissolved in ultrapure-water (10 mL). After this pre-gel solution was soaked in iced water in nitrogen atmosphere for 30 min, ammonium persulfate (10 mg) as an initiator was mixed, and microgels were prepared by suspension polymerization using liquid paraffin as oil phase at 4 °C for 6 hours. After gelation, they were thoroughly washed to remove unreacted compounds. The concentration of the introduced Ru(bpy)₃²⁺ in the gel was calculated by the absorption strength for the microgel suspension (2.1 × 10⁻¹ mM of Ru(bpy)₃²⁺). By comparing the absorption strength between the Pt colloidal solution and the microgel suspension, almost all of the Pt was introduced into the gel. Assuming that all of the Pt NPs was introduced in the gel, the suspension contained 1.4 × 10⁻² mM of Pt. Hydrogel mesh size at swollen state typically have a distribution around 2-6 nm from the analysis by scanning microscopic light scattering.

Measurements of the Swelling Ratio and Transmittance. The swelling ratio for the gel was measured as follows. The gel sample was inserted into a water-jacketed microcell together with the mixed solution. The temperature was controlled by circulating thermo-stated water through the water-jacket around the cell. The gel diameter at equilibrium state was then determined as a function of temperature by using a microscope with a calibrated scale. Using these diameters, the swelling ratio of the volume was calculated. Also, the transmittance for the microgel suspension as a function of temperature was measured by UV-vis spectrophotometer (UV-2500PC, SHIMADZU) equipped with an electronically thermo-stated cell holder by raising the temperature at a rate of 1.0 °C min⁻¹.

Preparation of the Gel System for Visible Light Irradiation. The poly(NIPAAm-*co*-Ru(bpy)₃) gel containing Pt nanoparticles was soaked in the mixture of methylviologen (MV²⁺) / ethylenediaminetetra acetic acid (EDTA). The microgel suspensions in the reaction cell (width: 10 mm, depth: 10 mm, height: ca. 50 mm) were stirred sufficiently at each temperature for 1 day, and then visible light was irradiated to one side of the cell by using a 100 W halogen lamp with flat surface light source (TECHNO LIGHT KTS-100RSV, Kenko). At given times, the generated gas was collected and analyzed by gas chromatography (GC-8APT, SHIMADZU).

(S2)

Optical microscopic observation of microgels at swollen state and shrunken state.

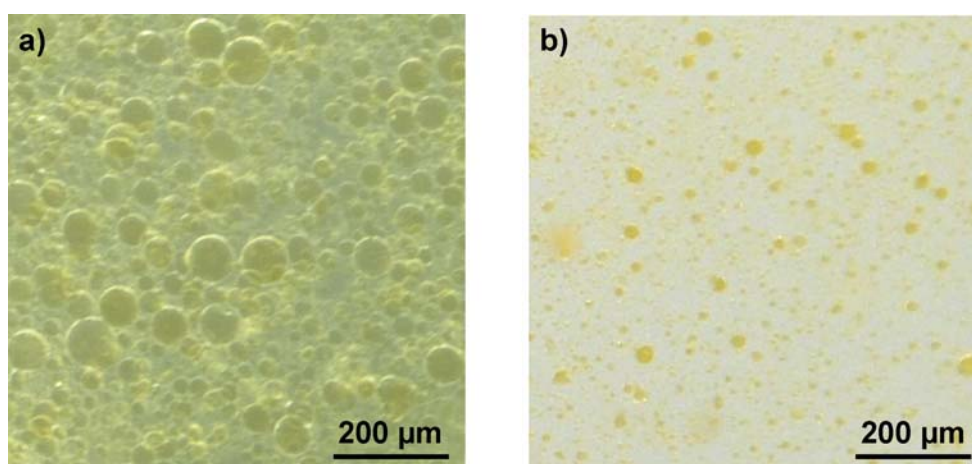


Figure S1. The microgel suspension in the mixture observed by optical microscopy at 20 °C (a) and 40 °C (b). [EDTA]₀ = 50 mM; [MV²⁺] = 5.0 mM.

Microgels in the mixture were swollen state at 20 °C, and shrunken state at 40 °C.

(S3)

Kinetics of the transmittance for the microgel suspension in shrinking/swelling process.

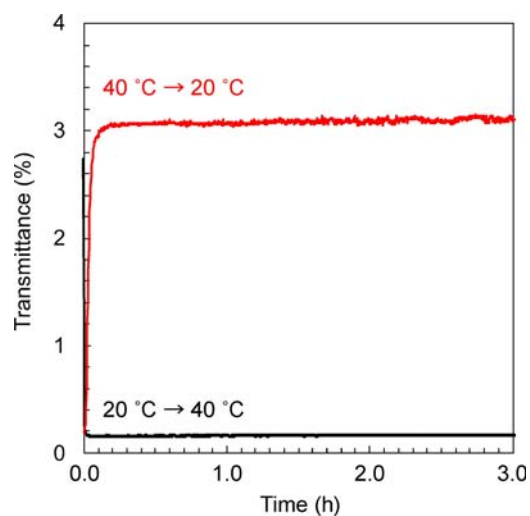


Figure S2. Time course of the transmittance for the microgel suspension with stepwise temperature changes. The total volume of the mixture: 3.0 mL, the total amount of gel particles: 20 mg. $[\text{EDTA}]_0 = 150 \text{ mM}$; $[\text{MV}^{2+}]_0 = 5.0 \text{ mM}$. $\lambda = 700 \text{ nm}$.

References

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